DOE/ET/14876--9

DE82 009371

CATALYSTS FOR UPGRADING COAL-DERIVED LIQUIDS

Quarterly Report for the Period
October 1 - December 31

Billy L. Crynes

The Oklahoma State University
School of Chemical Engineering
Stillwater, Oklahoma 74078

Date Submitted - January 19, 1982

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-AC22-79ET-14876

MASTER

NOTICE

**PORTIONS OF THIS REPORT ARE ILLEGIBLE. It
has been reproduced from the best available
copy to permit the broadest possible avail-
ability.**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy nor any of their employees, nor any of their contractors, sub-contractors, or their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned right.

NOT REPRODUCIBLE
FROM THE
-has been made available-

CATALYSTS FOR UP-GRADING COAL DERIVED LIQUIDS

(DE-14876-9)

ABSTRACT

Three catalysts have been identified for a three zone bed study. These three catalysts represent a small, medium and high pore catalyst system (Harshaw HT-115, Armak KF-153-S and Shell-214, respectively). A fifteen percent SRC in process solvent mixture was prepared for testing, and a micro-filtration apparatus for determining asphaltene content of the coal liquids was set up.

A parallel catalyst fouling model has been developed to interpret the experimental observations for hydrotreating SRC oil mixture in a trickle bed reactor. The model is significant because: 1) a variable diffusivity as a function of coke content is incorporated, 2) coke content profiles both within a pellet and the reactor bed are predicted with time and space, 3) catalyst activity is related to coke content, thus with time and space also, and 4) the model is supported by experimental data. Some spent catalysts were analyzed for carbon profiles within the pellets with a scanning Auger microscope in a commercial laboratory. The results are qualitative in nature, but are consistent with the fouling model predictions.

In experiments using from 0 up to 200 ppm titanocene dichloride, the results indicated that the presence of the titanocene dichloride slightly improved hydrogenation, hydrodenitrogenation and hydrodeoxygenation. Little could be determined from the hydrodesulfurization data. No consistent trends existed between catalyst activities and surface area, pore volume and coke content of the spent catalysts after processing the oils doctored with the titanocene dichloride. The fate of the titanium ions appears to be that of a water soluble compound found in the aqueous phase of the reactor products.

OBJECTIVE AND SCOPE OF WORK

The goal of this program is to investigate catalysts for upgrading liquids derived from coal-to-oil processes.

This research has the following technical objectives:

1. Investigate mechanisms responsible for rapid initial catalyst deactivation.
2. Study use of "throw away" catalysts and staged catalyst beds in hydroprocessing of coal liquids.

The investigation shall consist of the following tasks:

- Task 1-a. Inexpensive "throw away" type catalyst for coal liquids upgrading shall be investigated for reactor guard chamber service
- Task 1-b. Reactors packed with mixtures of catalyst types and zoned catalyst configurations shall be evaluated.
- Task 2-a. Catalyst life tests shall be conducted using a standard Ni-Mo/alumina hydroprocessing catalyst in the existing catalyst life test unit.
- Task 2-b. Changes in catalyst properties, including surface area, pore size distribution, pore volume, and coke and inorganics accumulation shall be measured as a function of coal-liquid contact time.
- Task 2-c. The Ni-Mo/alumina catalyst tested in Task 2-a shall be regenerated by oxidation, and tested for activity recovery.

SUMMARY OF PROGRESS TO DATE

The following chart summarizes the progress to date. Task 2-c activities are not as far along as scheduled. With the remaining resources and personnel, we will probably not do much more in this task area. The other tasks are progressing as scheduled.

As of December 31, 1981, 83% of the total budget has been expended (\$150,800). This is a somewhat accelerated expenditure rate caused by excess supplies costs. The subcategories expenditure of supplies and equipment is overspent and is counterbalanced in part by under expenditures in salaries.

PROGRESS SUMMARY AS OF DECEMBER 31, 1981

Scheduled

Progress

* Project start date is October 1, 1979

DESCRIPTION OF TECHNICAL PROGRESS

Task 1 - Throw Away and Zoned Catalyst Systems (O. K. Bhan)

Three commercial Ni-Mo-Al₂O₃ catalysts (Harshaw HT-115, Armak KF-153-S, Shell-214) were selected for use in zonal catalyst bed experiments. The physical properties of these catalysts were reported earlier.* These catalysts represent three distinct pore-size ranges available among commercial catalysts. Harshaw HT-115 is a large pore size catalyst with most frequent pore diameter (as determined by mercury penetration) of 17.0 nm. Armak KF-153-S represents a small pore size catalyst with most frequent pore diameter of 5.0 nm. Shell-214 represents medium pore size range of 11.0 nm. All these catalysts are 1.6 mm extrudes with similar metal loadings (3% NiO and 15% MoO₃). Experimental runs with catalyst and temperature sequencing through the reactor bed are planned using these catalysts.

A fifteen gallon mixture of 15% SRC (solid at room temperature) in process solvent was prepared. Care was taken for complete dissolution of SRC in the process solvent. SRC was gradually added to the solvent with constant stirring. The mixture was stirred for 12 hours at room temperature, after which the temperature was gradually raised and maintained at 125C for a period of 24 hours. Precautions were taken for minimum light fraction loss. The hot mixture was filtered through a 50 mesh size screen and stored in five gallon drums. Analyses of this feedstock will be presented in the next report.

A new sampling system for removal of 2-3 cm³ of liquid samples between the various trickle-bed reactor zones was tested at 7.0 MPa and room temperature using a light coal-derived liquid (simulating actual feedstock at higher temperatures). A 2-3 cm³ liquid sample was collected over a period of 2-3 minutes at a pump feed rate of 10×10^{-4} m³/hr. This system can be operated at temperatures as high as 450C and pressures up to 13.9 MPa. Such a sample represents the instantaneous liquid properties from the trickle-bed reactor zones.

A micro-filtration apparatus for determining asphaltene content of coal-derived liquids was set up. Teflon filters of 10µm pore size are used to separate asphaltene fraction from a mixture of coal liquids in a suitable solvent.

Work is being carried out on the construction of the new reactor system. Details of this system were presented in the previous report. This reactor system will be operational in the coming quarter.

* Quarterly Report for the period July 1 - September 30, 1981, DOE-14876-8.

Task 2 - Catalyst Life Studies (H. J. Chang)

During this reporting quarter, a parallel fouling model has been developed to interpret experimental observations for hydrotreating a SRC oil mixture in a trickle-bed reactor over the commercial Shell 324 NiMo/Al catalyst. The properties of the oil feedstock and the catalyst are shown in Tables I and II and in Figure 1.

The experimental conditions of the runs from which the data were generated are described in Table III. More details of these runs have been presented in Quarterly Report DOE-14876-8 for period July 1 to September 30, 1981.

The model is significant because: 1) a variable diffusivity as a function of coke content is incorporated, 2) coke content profiles both within a pellet and the reactor bed are predicted with time and space, 3) catalyst activity is related to coke content, thus with time and space also, and 4) the model is supported by experimental data.

A paper which has been submitted to the 7th International Symposium on Chemical Reaction Engineering to be held in Boston in the coming October is attached (Appendix A). This paper presents part of this work and includes (1) the experimental results, (2) the model development, (3) catalyst coke profiles in the trickle bed reactor for four experimental runs, (4) average catalyst coke content over the reactor versus time on stream, (5) catalyst activity versus average catalyst coke content over the reactor, and (6) most frequent pore diameter versus catalyst coke content.

The constants which were used in the model to predict the experimental results are shown in Table IV. Additional information on the catalyst activity versus time on stream and coke profiles within catalyst pellets will be discussed later.

Figures 2 and 3 show the catalyst activity (in terms of hydrogen or nitrogen contents in the product oil) versus time on stream. The experimental results can be predicted excellently by the model. Note that the experimental runs with different liquid volume hourly space time (LVHST) have been normalized to a LVHST of 2.50 hours according to the model of simple first order reactions and ideal plug flow.

Some spent catalysts were analyzed for carbon profiles within the pellets with a scanning Auger microscope (SAM) in a commercial laboratory. The complete results are listed in Table V. Note that the highest carbon content is around 80 atom%, whereas essentially no nitrogen (not shown in the table) was detected, which means that the nitrogen content on the spent catalyst is lower than 1 atom%. Furthermore, the nickel was not detected either, even in the freshly presulfided catalyst.

Figure 4 presents the precisions of the SAM analyses over the catalyst pellets from the same section of a run. Note that the SAM analyses should

TABLE I
PROPERTIES OF FEEDSTOCK

Feedstock	SRC ^a	
Total liquid density @ 21C (70F) kg/m ³	1129	
Normal boiling point ^b ,	<u>C</u>	<u>F</u>
IBP	242	(468)
5 vol.%	258	(497)
10	273	(523)
20	288	(550)
30	303	(578)
40	322	(612)
50	344	(652)
60	382	(719)
70	439	(823)
End point	454	(850)
Recovery, wt%	67	
Residue, wt%	32	
Loss, wt%	1	
Elemental composition, wt%		
Total liquid		
C	87.23	
H	6.73	
N	1.40	
S	0.50	
H/C atom	0.93	
Ash	0.097	
(454C ⁺) (850F ⁺)		
C	87.91	
H	5.41	
N	2.27	
S	0.65	
H/C atom	0.74	
(454C ⁺) (850F ⁻)		
C	87.92	
H	7.51	
N	0.88	
S	0.31	
H/C atom	1.03	

a. A mixture of 30 wt% SRC-I in 70 wt% process solvent

b. Determined from ASTM D1160 at 2.67kPa (20 mm Hg) vacuum.

TABLE II
CATALYST PROPERTIES

Catalyst Code	Shell 324
Chemical Composition, wt%	
NiO	3.4 (3.4)*
MoO ₃	19.3 (19.8)
Physical Properties	
Geometry	1.6mm (1/16") extrudate
Reactor density, kg/m ³	790.
Surface area, m ² /kg	146 x 10 ³ (150 x 10 ³)
Pore volume, m ³ /kg	4.2 x 10 ⁻⁴ (4.8 x 10 ⁻⁴)
Most frequent	
Pore diameter, nm	11.8 (118 Å)
Pore size distribution, **	
% pore volume in pore diameter, nm	%
3.5-7.0	12
7.0-10.0	21
10.0-15.0	57
15.0-20.0	2
20.0-40.0	1
40.0-60.0	1
>60.0	6
Total	100

*Values in the parentheses are vendor's data.

**See Figure 1 for more details.

TABLE III
EXPERIMENTAL RUN CONDITIONS

Reactor	CLTU II
Catalyst	Shell 324 (Table II)
Temperature	399C (750F)
Pressure	13.9 MPa (2000 psig)
Hydrogen Flow	1781 Std. m ³ H ₂ /m ³ Oil (10,000 SCF/Bbl)

<u>Run Series</u>	<u>Feedstock</u> *	<u>LVHST</u>	<u>Hours on Oil</u>
LTY	SRC	1.88	153
LTV	SRC	2.16-2.43	97
LTW	SRC	2.93	30
LTG	SRC	2.50	19
LTX	SRC	2.50	6
LTZ	SRC	2.50	1

* See Table I.

TABLE IV
CONSTANTS* USED IN MODEL PREDICTIONS

Feedstock density:	$\rho_A = 1.13 \times 10^3 \text{ kg/m}^3$
Catalyst bulk density:	$\rho_P = 1.42 \times 10^3 \text{ kg/m}^3$
Catalyst packed density:	$\rho_b = 0.78 \times 10^3 \text{ kg/m}^3$
Coke density:	$\rho_q = 0.80 \times 10^3 \text{ kg/m}^3$
Catalyst pellet porosity:	$\epsilon_P = 0.60$
Catalyst bed porosity:	$\epsilon_b = 0.78$
Feedstock hydrogen content:	$C_{Ao,H} = 1.40 \text{ wt\%}$
Feedstock nitrogen content:	$C_{Ao,N} = 6.73 \text{ wt\%}$
Maximum coke content:	$Q_M = 0.34 \text{ kg-coke/kg-catalyst}$
Equivalent radius of the catalyst pellet:	$r_e = 1.71 \times 10^{-3} \text{ m}$
Most frequent pore diameter of the freshly sulfided catalyst:	$PD = 11.0 \text{ nm}$
Reactor length:	$L = 0.5 \text{ m}$

* Experimentally determined.

TABLE V
SUMMARY OF THE RESULTS FROM SAM ANALYSES

Run	Sec.	Radius mm	Atom%				
			Sulfur	Moly.	Carbon	Oxygen	Aluminum
LTY	1	0.800	0.00	0.00	15.94	41.71	39.10
LTY	1	0.772	3.19	2.80	16.37	28.13	49.59
LTY	1	0.744	4.93	2.91	15.74	41.68	35.25
LTY	1	0.000	14.22	3.26	16.78	32.71	31.77
LTY	1	0.800	6.63	1.96	34.06	26.62	28.62
LTY	1	0.780	11.09	2.43	32.85	27.38	23.61
LTY	1	0.760	12.19	2.80	28.25	26.57	28.38
LTY	1	0.720	7.08	2.61	26.78	22.96	26.90
LTY	1	0.000	14.35	3.19	19.13	32.84	30.49
LTY	1	0.800	15.59	1.06	57.16	19.05	7.14
LTY	1	0.780	15.75	6.42	51.99	18.61	7.22
LTY	1	0.760	12.87	4.23	43.19	25.41	14.29
LTY	1	0.720	11.46	1.00	44.10	24.50	17.00
LTY	1	0.000	13.25	4.87	32.90	29.24	19.74
LTY	2	0.800	2.89	5.16	29.16	36.67	26.10
LTY	2	0.780	15.38	3.22	15.13	33.66	32.65
LTY	2	0.760	11.09	2.58	16.27	34.09	35.96
LTY	2	0.720	11.03	3.09	18.88	33.70	33.32
LTY	2	0.000	11.18	2.28	17.43	34.51	34.60
LTY	3	0.800	13.71	3.26	37.52	24.63	20.89
LTY	3	0.780	13.28	3.38	25.57	29.22	28.54
LTY	3	0.760	11.82	3.06	27.57	27.57	29.98
LTY	3	0.720	10.39	3.95	26.08	28.45	31.12
LTY	3	0.000	13.30	2.81	21.49	31.60	30.81
LTY	4	0.720	12.25	1.79	54.01	23.64	8.31
LTY	4	0.000	9.59	2.79	18.08	37.51	32.03
LTY	5	0.800	3.24	1.54	16.62	38.78	39.82
LTY	5	0.780	9.54	3.12	20.07	32.92	33.87
LTY	5	0.760	9.25	2.47	37.11	26.22	22.27
LTY	5	0.720	7.25	2.46	27.53	30.26	30.69
LTY	5	0.400	8.54	2.84	10.23	37.99	40.41
LTY	5	0.000	7.98	3.72	6.70	39.71	41.89

TABLE V
SUMMARY OF THE RESULTS FROM SAM ANALYSES
(Continued)

Run	Sec.	Radius mm	Atom%				
			Sulfur	Moly.	Carbon	Oxygen	Aluminum
LTW	1	0.800	8.44	0.00	64.96	17.32	0.00
LTW	1	0.786	11.58	3.47	20.85	29.89	34.21
LTW	1	0.772	11.97	2.85	9.22	37.56	38.41
LTW	1	0.744	10.19	2.64	12.39	36.46	38.34
LTW	1	0.400	14.36	4.34	7.81	35.27	38.22
LTW	1	0.000	16.49	3.21	5.77	38.47	36.07
LTW	5	0.800	12.30	3.63	22.86	32.65	28.57
LTW	5	0.780	13.87	4.65	15.71	36.31	29.46
LTW	5	0.760	16.59	5.33	10.79	39.18	28.11
LTW	5	0.720	13.36	4.35	15.67	37.22	29.39
LTW	5	0.000	12.82	5.14	12.34	41.13	27.95
LTX	1	0.800	4.38	0.00	78.75	16.89	0.00
LTX	1	0.786	6.65	0.00	71.72	21.63	0.00
LTX	1	0.772	6.18	0.00	39.04	28.47	26.31
LTX	1	0.744	7.90	2.46	16.60	39.47	33.72
LTX	1	0.000	12.28	3.68	2.22	43.48	38.35
LTX	2	0.800	4.82	1.65	26.72	29.69	37.12
LTX	2	0.786	6.37	2.22	23.93	30.48	36.64
LTX	2	0.772	6.63	2.10	16.07	35.30	39.89
LTX	2	0.744	6.67	2.50	19.83	32.14	38.86
LTX	2	0.400	7.63	2.66	10.41	35.15	44.18
LTX	2	0.000	10.31	3.27	3.36	39.76	43.31
LTX	3	0.800	9.10	2.36	31.14	26.89	30.52
LTX	3	0.786	12.02	2.98	6.04	39.36	39.61
LTX	3	0.772	12.37	3.24	2.19	41.13	41.07
LTX	3	0.744	13.60	3.61	3.25	39.23	40.32
LTX	3	0.000	13.15	4.17	3.75	42.53	38.09
LTX	3	0.000	13.15	4.17	3.75	42.53	38.09
LTX	3	0.744	11.71	3.60	2.77	39.45	42.47
LTX	3	0.772	9.49	2.88	7.26	36.63	43.74
LTX	3	0.786	8.69	4.13	8.36	39.63	39.19
LTX	3	0.800	7.58	1.80	18.65	33.79	35.74
LTX	4	0.800	7.30	2.52	6.82	48.45	38.32
LTX	4	0.786	3.69	2.34	3.16	48.40	42.42
LTX	4	0.772	6.08	2.41	3.47	44.19	43.86
LTX	4	0.744	9.48	3.38	6.08	39.02	42.04
LTX	4	0.000	11.49	3.83	2.95	43.93	37.80

TABLE V
SUMMARY OF THE RESULTS FROM SAM ANALYSES
(Continued)

13

Run	Sec.	Radius mm	Atom%				
			Sulfur	Moly.	Carbon	Oxygen	Aluminum
LTX	5	0.800	19.49	25.93	33.33	68.89	0.00
LTX	5	0.786	6.55	2.02	0.00	45.40	46.00
LTX	5	0.772	8.95	0.00	13.51	42.33	30.39
LTX	5	0.000	9.67	3.78	2.84	37.82	43.44
LTF	*	0.800	3.13	1.59	15.37	45.16	33.51
LTF	*	0.772	4.29	1.95	12.32	45.16	36.29
LTF	*	0.744	1.74	4.95	1.98	46.19	39.44
LTF	*	0.000	3.89	5.24	3.33	46.22	40.04
LTZ	1	0.800	10.82	4.02	6.04	40.64	38.48
LTZ	1	0.780	11.66	4.34	3.90	45.96	34.15
LTZ	1	0.760	11.73	4.18	2.51	45.14	36.44
LTZ	1	0.720	10.81	4.69	2.41	41.41	40.70
LTZ	1	0.000	11.75	4.51	2.31	44.46	36.97
LTZ	5	0.800	8.11	3.19	11.48	37.22	39.03
LTZ	5	0.780	9.79	2.70	4.86	41.61	41.04
LTZ	5	0.760	11.61	3.88	1.40	44.25	39.30
LTZ	5	0.720	11.31	4.40	2.64	40.47	39.59
LTZ	5	0.000	10.65	3.30	3.56	42.38	40.10
LTB	1	0.800	3.92	2.10	31.44	25.99	36.55
LTB	1	0.786	3.89	1.75	18.93	34.01	41.41
LTB	1	0.772	4.20	1.80	5.39	43.13	45.49
LTB	1	0.000	9.49	2.85	7.69	36.73	43.25
LTB	5	0.800	14.75	10.36	30.28	23.29	15.28
LTB	5	0.786	16.81	5.33	17.81	29.23	30.82
LTB	5	0.772	13.53	3.09	18.06	31.48	33.85
LTB	5	0.744	3.65	2.89	29.14	30.18	34.15
LTB	5	0.000	10.54	2.67	10.83	36.49	39.47
FRS	**	0.800	13.20	5.17	0.00	44.28	37.36
FRS	**	0.780	12.30	4.55	0.00	43.67	39.48
FRS	**	0.760	13.84	5.18	0.00	43.86	37.12
FRS	**	0.720	11.53	5.16	0.00	44.12	39.19
FRS	**	0.000	13.88	4.85	0.00	41.46	39.89
FRS	**	0.800	10.65	5.59	0.00	41.91	41.85
FRS	**	0.780	9.82	5.59	0.00	43.25	41.33
FRS	**	0.760	9.23	6.02	0.00	42.87	41.88
FRS	**	0.720	12.72	5.87	0.00	41.98	39.53
FRS	**	0.000	6.77	6.11	0.00	42.34	44.78

*Not separated into sections

**Freshly sulfided catalysts

CATALYST: FRESH SHELL 324

DISTRIBUTION= $\Delta V / \Delta \log(D)$
WHERE V=PORE VOLUME, D=DIAMETER

FIGURE 1. PORE SIZE DISTRIBUTION

FIGURE 2. CATALYST ACTIVITY VERSUS TIME ON STREAM

FIGURE 3. CATALYST ACTIVITY VERSUS TIME ON STREAM

SPENT CATALYST FROM SETION 1, RUN LTY

LEGEND: SYMBOL Δ Δ Δ SAMPLE 1 □ □ □ SAMPLE 2 + + + SAMPLE 3

FIGURE 4. PRECISIONS OF THE CARBON PROFILE ANALYSES

be regarded as qualitative results only because: 1) SAM is a very surface sensitive instrument, it can only detect the atoms within the depth of 1 to 4 nm from the surface, this results in exaggeratedly high contents for the deposited atoms; and 2) catalysts are heterogeneous in nature and may be different from pellet to pellet.

Figures 5 to 9 show the coke profiles within catalyst pellets for five representative samples. The profiles predicted by the model are also presented for comparison. The trends are consistent even though the experimental data are qualitative and somewhat scattered.

Figure 10 summarizes the coke profiles predicted by the model for the catalysts shown in Figures 5-9 to demonstrate the response of coke profile to time on stream. The figure shows that coke deposition becomes heavier both at inside and outside of the catalyst pellet as time on stream increases.

Work Forecast

During the coming quarter, the model will be extended to predict the effects of catalyst pellet sizes and pore sizes on the trickle bed reactor performance during hydrotreating the SRC oil over the Shell 324 catalyst.

SPENT CATALYST FROM SECTION 3, RUN LTY

FIGURE 5. COKE PROFILE IN THE CATALYST PELLET

SPENT CATALYST FROM SECTION 1, RUN LTW

FIGURE 6. COKE PROFILE IN THE CATALYST PELLET

SPENT CATALYST FROM SECTION 1, RUN LTX

FIGURE 7. COKE PROFILE IN THE CATALYST PELLETS

SPENT CATALYST FROM SECTION 5, RUN LTW

FIGURE 8. COKE PROFILE IN THE CATALYST PELLETS

SPENT CATALYST FROM SECTION 5, RUN LTZ

FIGURE 9. COKE PROFILE IN THE CATALYST PELLET

FIGURE 10. COKE PROFILES IN THE CATALYST PELLETS

Task 2. Catalyst Life Studies (W. S. Chan) (Faculty Advisor: Prof. M. Seapan)

During this reporting quarter, five experimental runs (TME 6,7,8,9 and 10) were made. The individual run conditions are shown in Table VI.

Complete data are now available for TME 4,5 and 6, and are shown in Tables VII-IX. Results from TME 7-10 will be available next quarter. The effects of titanocene dichloride on the catalyst and hydrotreated oils can be seen from the brief summary comparison between TME 4,5 and 6 listed in Table X. Runs TME 4 and 6 with doctored titanocene dichloride have improved hydrogenation, hydrodeoxygenation and also hydrodenitrogenation before restriction of hydrogen flow happened to TME 4. As for hydrodesulfurization, TME 4 has comparatively better sulfur removal than TME 5 and 6.

Table XI shows surface area, pore volume and coke content of spent catalysts. No consistent trend between these data and catalyst activities was found. Coke accumulation decreases from top to the bottom of the bed. Distillation data for feedstock and sample #3 of TME 4,5 and 6 are shown in Table XII. The higher percentage of low boiling point products in TME 4 and 6 suggests improved cracking for feedstocks with doctored titanocene dichloride.

A polymerized titanium compound was indicated in the last report to form above the catalyst bed in TME 2-4. Analysis shows that the titanium content in TME 4 and 6 are comparable: 3.63 wt% for TME 4 and 3.43 wt% for TME 6. Polymer-attached titanocene was reported to be used in the catalysis of olefin hydrogenation.*

The fate of the added titanocene dichloride in the hydrotreating process is being studied. The analyses of titanium in product oils generated in TME 4 and 6 show only trace amounts left in the oil phase. Titanium analyses have not yet been made for the aqueous phase. The aqueous phase is slightly basic (pH=8), and once separated from the oil phase, exposure to air results in white crystal formation. Analysis showed the crystals contained no N,C and H. Effort will be concentrated on the analysis of titanium in the aqueous phase.

Qualitative analysis for chloride was done on the aqueous phase separated from oil, and on the effluent gas (absorbed in NaOH solution). The precipitate of silver chloride confirmed the existence of chloride in both the aqueous phase and gas phase. The chloride from titanium was likely converted into HCl during hydrotreating and dissolved in the aqueous phase or carried in the effluent gas. No attempt has been made to identify chlorine compounds in the hydrotreated oil.

* (1) Bonds, W. D., Jr., Brubaker, C. H., Jr., Chandrasekaran, E. S. Gibbons, C., Grubbs, R. H., and Kroll, L. C., J. Am. Chem. Soc., 97, 2128 (1975).

(2) Chandrasekaran, E. S., Grubbs., R. H. and Brubaker, C. H., Jr., J. Organometal. Chem., 120, 49 (1976).

SUMMARY

1. Titanocene dichloride doctored in the feedstock improved hydrogenation, hydrodenitrogenation and hydrodeoxygenation.
2. No consistent trends exist between catalyst activities and surface area, pore volume and coke content of spent catalysts.
3. Titanium contents in the carbonaceous material formed in TME 4 and 6 are comparable.

WORK FORECAST

A scheduled experimental run TME 11 will be made in January, then efforts will be concentrated on the analyses of samples to evaluate the effects of titanocene dichloride on the catalyst and the hydrotreating process.

TABLE VI
RUN CONDITIONS

1. Reactor: trickle bed reactor, EN-1
2. Feedstock:
 - (a) SRC light oil + 50ppm titanocene dichloride (TME 8)
 - (b) SRC light oil + 100ppm titanocene dichloride (TME 6,7,10)
 - (c) SRC light oil + 200ppm titanocene dichloride (TME 9)
3. Catalyst:
 - (a) Shell 324 (TME 6,8,9,10)
 - (b) No catalyst but glass beads (TME 7)
4. Temperature:
 - (a) 375C (707F) (TME 6,7,8,10)
 - (b) 365C (689F) (TME 9)
5. Pressure: 10.4 MPa (1500 psig)
6. Hydrogen flow: 1425 Standard $\text{m}^3\text{H}_2/\text{m}^3\text{Oil}$ (8,000SCF/Bbl)
7. LVHST: 0.58 hrs.
8. Run duration:
 - (a) 66 hrs. (TME 6,9,10)
 - (b) 24 hrs. (TME 7)
 - (c) 54 hrs. (TME 8)

NOTE: Scheduled run duration for TME 8 was 66 hrs., but because a rupture disk failed the run was shut down prematurely.

TABLE VII

RESULTS FROM RUN TME 4 WITH SHELL 324 CATALYST

FEEDSTOCK: SRC LIGHT OIL + 400 PPM TITANOCENE DICHLORIDE

Sample Number	Hrs ^a On Oil	Wt% ^b S	%S ^c Removal	Wt% ^b N	%N ^c Removal	ppm Ti	%Ti ^c Removal	H/C Atom Ratio	Aqueous ^d phase (ml)
TME 4-1	6	0.23	30.3	---	---	27.0	93.3	---	11
TME 4-2	12	0.03	91.8	0.131	65.5	0	100	1.614	13
TME 4-3	18	0.01	97.0	0.098	75.8	0	100	1.800	14
TME 4-4	24	0.01	97.0	0.104	72.4	6.2	98.5	1.804	14
TME 4-5	30	0.04	87.9	0.215	56.6	9.1	97.7	1.737	10
TME 4-6	36	0.042	93.9	0.141	62.9	5.8	98.6	1.616	12
TME 4-7	42	0.04	87.9	0.182	52.1	5.8	98.6	1.647	11
TME 4-8	48	0.01	97.0	0.224	41.1	7.1	98.2	1.715	11
TME 4-9	54	0.01	97.0	0.264	30.5	5.1	98.7	1.705	8
TME 4-10	60	0.03	91.8	0.317	16.6	9.2	97.7	1.666	6
TME 4-11	66	---	---	---	---	8.4	97.9	---	5

- a. Total hours which the catalyst has been contacted with oil at reaction temperature.
- b. Percent of sulfur, nitrogen in liquid product.
- c. % Removal = $100 \times (\text{fraction in feed less fraction in product}) / (\text{fraction in feed})$.
- d. Volume of aqueous phase in product sample.

TABLE VIII
RESULTS FROM RUN TME 5 WITH SHELL 324 CATALYST
FEEDSTOCK = SRC LIGHT OIL

Sample Number	Hrs ^a On Oil	Wt% ^b S	%S ^c Removal	Wt% ^b N	%N ^c Removal	ppm Ti	%Ti ^c Removal	H/C Atom Ratio	Aqueous ^d phase (ml)
TME 5-1	6	0.07	81.6	0.153	59.7	0	0	1.636	9
TME 5-2	12	0.07	81.6	0.162	57.9	0	0	1.650	8
TME 5-3	18	0.08	79.0	0.164	56.8	0	0	1.615	7
TME 5-4	24	0.06	84.2	0.166	56.3	0	0	1.633	7
TME 5-5	30	0.08	79.0	0.168	55.8	0	0	1.617	7
TME 5-6	36	0.06	84.2	0.188	50.5	0	0	1.616	7
TME 5-7	42	0.10	74.0	0.227	40.3	0	0	1.622	6
TME 5-8	48	0.05	86.8	0.233	38.7	0	0	1.580	4.5
TME 5-9	54	0.04	89.5	0.264	30.5	0	0	1.540	4.5
TME 5-10	60	0.03	92.1	0.224	41.1	0	0	1.585	4
TME 5-11	66	0.05	86.8	0.263	30.8	0	0	1.612	4

- a. Total hours which the catalyst has been contacted with oil at reaction temperature.
b. Percent of sulfur, nitrogen in liquid product.
c. % Removal = $100 \times (\text{fraction in feed} - \text{fraction in product}) / (\text{fraction in feed})$.
d. Volume of aqueous phase in product sample.

TABLE IX

RESULTS FROM RUN TME 6 WITH SHELL 324 CATALYST

FEEDSTOCK = SRC LIGHT OIL + 100 PPM TITANOCENE DICHLORIDE

Sample Number	Hrs ^a On Oil	Wt% ^b S	%S ^c Removal	Wt% ^b N	%N ^c Removal	ppm Ti	%Ti ^c Removal	H/C Atom Ratio	Aqueous ^d phase (ml)
TME 6-1	6	0.07	81.6	0.014	96.3	0	100	1.836	14
TME 6-2	12	0.02	94.8	0.025	93.4	0	100	1.898	17.5
TME 6-3	18	0.34	10.5	0.030	92.1	0	100	1.879	16.5
TME 6-4	24	0.14	63.2	0.020	94.7	0	100	1.877	16.5
TME 6-5	30	0.13	65.8	0.023	93.9	0	100	1.856	16.5
TME 6-6	36	0.00	100	0.051	86.6	0	100	1.880	16.5
TME 6-7	42	0.05	86.8	0.040	89.5	0	100	1.836	16.5
TME 6-8	48	0.03	92.1	0.048	87.4	0	100	1.825	16
TME 6-9	54	0.07	81.6	0.042	88.9	0	100	1.828	16
TME 6-10	60	0.02	96.8	0.044	88.4	0	100	1.815	16
TME 6-11	66	0.15	60.5	0.028	92.6	0	100	1.772	16

a. Total hours which the catalyst has been contacted with oil at reaction temperature.

b. Percent of sulfur, nitrogen in liquid product.

c. % Removal = $100 \times (\text{fraction in feed} - \text{fraction in product}) / (\text{fraction in feed})$.

d. Volume of aqueous phase in product sample.

TABLE X
COMPARISON BETWEEN TME 4,5 AND 6

- a. Hydrogenation (or H/C atomic ratio)

TME 6 > TME 4 > TME 5

- b. Hydrodenitrogenation

TME 6 > TME 4 > TME 5 (Before restriction of hydrogen flow happened to TME 4)

TME 4 $\approx$ TME 5 (After restriction happened)

- ### c. Hydrodesulfurization

TME 4 > TME 5 & TME 6

- d. Hydrodeoxygenation (as measured by the volume of aqueous phase)

TME 6 > TME 4 > TME 5

- e. Coke Content.

$$\text{TME } 4 < \text{TME } 6 < \text{TME } 5$$

- f. Surface area and pore volume

No consistent trend.

TABLE XI
ANALYSIS OF SPENT CATALYST

Sample Number	Zone In Catalyst Bed	Surface Area $10^3 \text{ m}^2/\text{kg}$	Pore Volume $10^{-3} \text{ m}^3/\text{kg}$	Ti (a) Wt%	Coke Content Wt%
TME 4	Top	141	0.268	1.64	11.84
	Middle	131	0.236	0.46	4.70
	Bottom	115	0.210	0.07	0.78
TME 5	Top	137	0.221	0	11.40
	Middle	119	0.287	0	11.90
	Bottom	135	0.363	0	6.46
TME 6	Top	(b)	(b)	(b)	(b)
	Middle	112	0.342	0.04	7.70
	Bottom	127	0.268	0	5.30

a. Ti concentration is analyzed by "Phillips X-Ray Spectrometer XRG-300".

b. Not available.

TABLE XII
DISTILLATION DATA

VOL %	FEEDSTOCK		TME 4 Sample #3		TME 5 Sample #3		TME 6 Sample #3	
	C	F	C	F	C	F	C	F
IBP	88	190	96	205	75	167	92	197
10	172	341	107	224	82	180	102	216
20	176	349	114	238	140	284	106	223
30	179	354	118	245	167	333	116	241
40	181	358	158	316	174	346	144	292
50	183	361	174	345	178	353	174	345
60	184	364	181	358	181	358	184	363
70	187	368	187	369	184	364	188	371
80	189	373	194	381	189	373	193	380
90	194	332	204	399	197	386	207	405
END POINT	199	390	211	412	208	407	214	418
Recovery	98		98		98		98	
Residue	1		1		1		1	
Loss	1		1		1		1	

APPENDIX A

CATALYST DECAY DURING HYDROTREATMENT
OF A HEAVY COAL OIL

Hong Ju Chang, Mayis Seapan and Billy L. Crynes
School of Chemical Engineering
Oklahoma State University
Stillwater, OK 74078

Paper submitted to the
Seventh International Symposium on
Chemical Reaction Engineering
Boston, Massachusetts
October, 1982

CATALYST DECAY DURING HYDROTREATMENT OF A HEAVY COAL OIL

Hong Ju Chang, Mayis Seapan and Billy L. Crynes

School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74078

ABSTRACT

A trickle-bed reactor was used to study catalyst deactivation during hydrotreatment of a mixture of 30 wt% SRC and process solvent. The catalyst was Shell 324, NiMo/Al having monodispersed, medium pore diameters. The catalyst zones of the reactors were separated into five sections, and analyzed for pore sizes and coke contents. A parallel fouling model is developed to represent the experimental observations. Both model predictions and experimental results consistently show that: 1) the coking reactions are parallel to the main reactions, 2) hydrogenation and hydrodenitrogenation activities can be related to catalyst coke content with both time and space, and 3) the coke severely reduces the pore size and restricts the catalyst efficiency. The model is significant because it incorporates a variable diffusivity as a function of coke deposition, both time and space profiles for coke are predicted within pellet and reactor, activity is related to coke content, and the model is supported by experimental data.

INTRODUCTION

Catalyst deactivation by coke deposition is a major concern in upgrading coal-derived oils. Coke forms as a result of a sequence of side reactions which may be simplified as follows:

If coke forms mainly by routes 1 only, then this is parallel fouling; if mainly by routes 2 and 3, it is series; and if equally by all three routes, then it is independent fouling.

John et al. (1) in distillates catalytic cracking studies concluded that coke on the catalyst cannot be a measure of activity. However, in an earlier work by Voorhies (2), a linear correlation between conversion and coke on catalyst for fixed-bed catalytic cracking was derived. Rudershausen and Watson (3) also observed the similar behavior. Coke on catalyst can reduce the activity by covering the active sites and blocking the pores. The effects of pore size on catalyst performance during hydrotreating coal oils in trickle-bed reactors have been studied experimentally by Ahmed and Crynes (4) and by Sooter (5). The pore size effects in other studies are also reported (6,7). Prasher et al. (8) observed that the effective diffusivities of oils in aged catalysts were severely reduced by coke deposition.

Theoretical work by Masamune and Smith (9), who applied active site coverage to account for intrinsic activity decay, predicted carbon profiles in a catalyst pellet as a function of time on stream and Thiele modulus. Their results show that the foulant deposition is heavier at the outside of the pellet for parallel fouling; whereas, deposition inside is heavier for series fouling. At a high Thiele modulus where diffusion limitation is severe, the foulant deposition is always heavier at the outside of the pellet regardless of the

mechanism. Essentially the same results were shown by Chiou and Olson (10) who extended Masamune and Smith's work to account for the effect of pore structure. Froment and Bischoff (11) developed a model to predict the conversions and coke profiles in a fixed-bed reactor by assuming several relationships between activity and bulk coke content in the catalyst pellet. The results show that coke deposition decreases toward reactor exit for parallel fouling but increases toward the exit for series fouling.

All of these models have been limited to only partial representation of catalyst coking-decaying phenomena in a fixed-bed reactor. No experimental data have shown consistency between the many features including fouling mechanism, catalyst activity, pore size and coke profiles in both the pellet and the trickle-bed reactor. In this study experimental data on coke contents, coke-time and position profiles, pore sizes and catalyst activities resulting from a trickle-bed reactor are presented to demonstrate the relationships and consistencies. A parallel fouling model based on active site coverage and pore blockage is developed and extended to the fixed-bed reactor performance of a catalyst processing a heavy coal oil.

EXPERIMENTAL

The oil feedstock used in this study was a 30 wt% SRC-I and 70 wt% process solvent mixture containing 87.2 wt% carbon, 6.73 wt% hydrogen, 1.40 wt% nitrogen, 0.50 wt% sulfur and 0.097 wt% ash, having an initial boiling point of 242C and with 32 wt% boiling at higher than 454C. The catalyst was Shell 324, a NiMo/Al catalyst having a surface area of $150 \times 10^3 \text{ m}^2/\text{kg}$, a pore volume of $0.42 \times 10^{-3} \text{ m}^3/\text{kg}$ and a narrow pore size distribution at 11.0 nm.

A 0.5 m by 0.013 m trickle-bed reactor equipped with automatic temperature, pressure and flow controls and adequate safety monitoring systems was used in this study. The catalyst was calcined and presulfided before startup. The nominal operational conditions were: temperature, 400C; pressure 13.9 MPa; liquid volume space time, 2.50 hours; and hydrogen-to-oil ratio, 1780 std. $\text{m}^3 \text{H}_2/\text{m}^3 \text{oil}$. During shutdown, the reactor was cooled quickly with a high flow of hydrogen to prevent excess coking. The used catalysts were separated into five sections, 0.1 meter each, extensively extracted with pyridine, and dried in a high vacuum oven. Thus, the coke content in this study is defined as pyridine insoluble carbonaceous material and was determined by oven combustion in air. Special care was taken to avoid moisture adsorption which could badly mask the actual values of coke contents. The pore volumes and pore sizes were measured with a Micromeritics Model 910 mercury porosimeter by assuming a contact angle of 130 degrees. Oil products were routinely analyzed for hydrogen and nitrogen contents with a Perkin-Elmer Model 240B elemental analyzer. More details on this experimental work have been reported by Crynes (12).

EXPERIMENTAL RESULTS

Six experimental runs were made at essentially the same operating conditions but with various durations to obtain parameters as functions of time on stream. Coke profile results are shown in Figure 1. Note that coke content is high at the reactor entrance and the slope of the profile gradually increases to a maximum then levels off (at 153 hours). The maximum activity

zone (low coke content) within the reactor gradually moves down to the reactor exit. This type of profile implies that the coking reactions fall into the parallel pattern shown by Froment and Bischoff (11). The coke contents from different sections of each run were averaged over the reactor, and the results are plotted in Figure 2. Most coke forms during the first 40 hours on stream. Note that during startup and within the first hour of operation, nearly 5 wt% coke has accumulated.

Figure 3 suggests a relationship between catalyst activity (in terms of hydrogen and nitrogen contents in the product oil) and coke content. Figure 4 shows that coke has severely blocked the pore mouths. These pore sizes have been experimentally determined and not calculated from a pore volume-surface area relationship. Additional Auger analyses support the bulk analysis results and further reveal that coke accumulates predominately within the outer edges of the pellets. With increasing time on stream, the coke penetrates more deeply within the pellet ultimately achieving a maximum value of 14 wt%.

DISCUSSION

A model based on parallel fouling was developed to represent these experimental observations. The following assumptions were made:

- (1) The reactions can be described by two simple first order parallel reactions (routes 1 and 2 of the scheme presented earlier):

- (2) Coking rate is much slower than the main reactions rate.
- (3) The reactor is isothermal throughout and is ideal plug flow.
- (4) There is a negligible mass transfer resistance external to the pellets.
- (5) Pores are filled with liquid throughout the reactions.
- (6) Effective diffusivity of the reactant versus pore size follows the Satterfield et al. correlation (13): $D_{Ae} = [D_{Ap} / \tau] [\text{Exp} (-4.6\lambda)]$ [1]
- (7) Pores are uniform and parallel to each other: $D = D_o (\epsilon_p / \epsilon_{po})^{1/2}$ [2]
- (8) The catalyst porosity is reduced by the coke: $\epsilon_p = \epsilon_{po} - Q_p (\rho_p / \rho_q)$ [3]

This model is significant because: 1) a variable diffusivity as a function of coke content is incorporated, 2) coke content profiles both within a pellet and the reactor bed are predicted with time and space, 3) catalyst activity is related to coke content, thus with time and space also, and 4) the model is supported by experimental data.

The conservation equations representing the intraparticle deactivation in non-dimensional form for spherical geometry are given as follow:

$$D \frac{\partial^2 y_p}{\partial x_p^2} + \frac{\partial D}{\partial x_p} \frac{\partial y_p}{\partial x_p} + \frac{2D}{x_p} \frac{\partial y_p}{\partial x_p} - h_A^2 (1-q_p)^m y_p - h_q^2 \epsilon \frac{\partial y_p}{\partial \theta_p} = 0 \quad [4]$$

$$\frac{\partial q_p}{\partial \theta_p} = (1 - q_p)^n y_p \quad \text{and} \quad D = \beta \epsilon \text{Exp} [-4.6\lambda_o / (1 - \gamma q_p)^{1/2}] \quad [5], [6]$$

Initial and boundary conditions are:

$$@ \theta_p = 0 \text{ and } 0 \leq x_p \leq 1, \quad y_p = 1, q_p = 0, \varepsilon = 1, D = 1 \quad [7]$$

$$@ x_p = 1 \text{ and } \theta_p > 0, \quad y_p = 1 \text{ also } @ x_p = 0 \text{ and } \theta_p > 0, \quad \frac{\partial y_p}{\partial x_p} = 0 \quad [8], [9]$$

The dimensionless equations over the reactor bed itself are:

$$\frac{\partial y_b}{\partial \theta_b} + E \frac{\partial y_b}{\partial x_b} + G \eta_A y_b = 0 \quad \text{and} \quad \frac{\partial q_b}{\partial \theta_b} = \eta_q y_b \quad [10], [11]$$

Initial and boundary conditions are:

$$@ \theta_b = 0 \text{ and } 0 \leq x_b \leq 1, \quad y_b = 1, q_b = 0 \quad \text{also} \quad [12]$$

$$@ x_b = 0 \text{ and } \theta_b > 0, \quad y_b = 1 \quad [13]$$

The effectiveness factors η_A and η_q , defined as the ratios of the actual reaction rates at time θ to the maximum reaction rates on a clean catalyst, are obtained numerically from equations [4] - [9]. An explicit finite difference method was used to solve the partial differential equations without further simplifications. Densities, porosities and clean catalyst pore diameters were measured experimentally. The maximum coke content is assumed to be that which fills the pore completely. The tortuosity is taken as 2.3, as discussed by Satterfield et al. (13).

The rate constants, bulk diffusivity, critical solute diameter and intrinsic rate decaying orders were varied to obtain the data fit. The resulting rate constants are $1.13 \times 10^{-6} \text{ m}^3/(\text{sec})(\text{kg-catalyst})$ for the main reaction, $0.948 \times 10^{-9} \text{ m}^3/(\text{sec})(\text{kg-catalyst})$ for the coking in terms of hydrogenation or $3.704 \times 10^{-9} \text{ m}^3/(\text{sec})(\text{kg-catalyst})$ in terms of hydrodenitrogenation. The critical solute diameter of 3.3 nm, bulk diffusivity of $0.55 \times 10^{-9} \text{ m}^2/\text{sec}$, orders of deactivation of half for the main reaction and second order for coking, and the corresponding Thiele modulus, 11.4, for the main reaction at clean catalyst conditions all fall within reasonable ranges which have been reported. Second order deactivation for the coking reaction indicates that the reaction may take dual sites, while the half order deactivation for the main reaction indicates that the small molecules less subjective to coking may still be able to access the sites restricted by coke.

The coke profiles in the reactor bed can be predicted excellently by the model as shown by the solid lines in Figure 1. Figure 2 shows good consistency is also obtained for the average coke content over the reactor bed versus time on stream. Note that within the time period of reactor startup plus one hour of operation, the average coke content of the reactor bed is already at about 5 wt%. The model cannot be applied to this startup and initial period with the rapid transients of temperature, activity "spike" and concentration. However, compensation for this interval can be made by a time translation of the model: a model time of 36 hours is fixed at an experimental time of zero. A temperature difference of more than 20C between the center of the

bed and outer wall of the reactor in the startup stage has been observed in our laboratory for some experiments. About three-fourths of this difference is across the catalyst bed itself. Startup of the reactor at reasonably lower temperatures in order to control the coke formation and to better maintain the catalyst activity is important, if not critical.

The model predicts that the dependencies of hydrogenation and hydrodenitrogenation activities on the reactor coke content are stronger than linear, and are satisfactorily supported by the experimental data as shown in Figure 3. The predicted pore size-coke content relationship is shown in Figure 4. The trend is consistent with the experimental data, although data at high coke loading lie above the predicted line. Two reasons may have contributed to this: 1) the contact angles for catalyst-mercury and coke-mercury may be different and 2) the mercury porosimetry method could be limited to measuring small pore sizes.

CONCLUSION

A parallel fouling model has been developed to represent experimental observations for hydrotreating a coal oil in a trickle-bed reactor over a commercial NiMo/Al catalyst. This model accurately predicts coke profiles with time and reactor position, and hydrogenation and hydrodenitrogenation as functions of coke content. The following conclusions can be drawn from this study.

- (1) Catalyst coke content is a good measure of activity. Both hydrogenation and hydrodenitrogenation can be related to coke content.
- (2) Coke severely reduces the pore sizes and restricts the catalyst efficiency.
- (3) Poorly controlled high temperatures during startup can result in excess coking reaction.
- (4) The catalytic coking reaction may require dual catalyst sites, whereas small size reactants which are less subjective to coking may be able to access the sites covered by the coke.

ACKNOWLEDGEMENTS

We acknowledge and appreciate the support provided for this study by the U.S. Department of Energy and Oklahoma State University.

NOMENCLATURE

C	=	Concentration of reactant in liquid, kg/m ³
D	=	Dimensionless effective diffusivity, D_{Ae}/D_{Aeo}
D_A, D_{Ae}	=	Bulk and effective diffusivity, m ² /sec
E, G	=	Dimensionless groups, $E = Q_M/C_{Af} k_q T$, $G = k_A \rho_b Q_M/C_{Af} k_q$
h	=	Thiele Modulus, $h_A = \gamma_e \sqrt{\rho_p k_A/D_{Aeo}}$, $h_q = \gamma_e \sqrt{k_q C_{Ab} \epsilon_{Po}/D_{Aeo} Q_M}$
k	=	Intrinsic rate constant, m ³ /(sec)(kg-catalyst)
L	=	Total Length of the reactor bed, m
m, n	=	Exponents of the main and the coking deactivations
PD	=	Most frequent pore diameter, nm

q	= Dimensionless coke content, Q/Q_M
Q,	= Coke contents, kg-coke/kg-catalyst, Q_M maximum coke content
r	= Radial position from the center of the catalyst pellet, m
r_e	= Equivalent radius of the catalyst pellet, m
SD	= Critical solute diameter, nm
T	= Liquid volume space time, sec.
t	= Time on stream, sec.
x	= Dimensionless position, $x_b = z/L$, $x_p = r/r_e$
y	= Dimensionless concentration, $y_b = C_{Ab}^p/C_{Af}$, $y_p = C_{Ap}/C_{Ab}$
z	= Longitudinal position in reactor bed from entrance, m.

Greek Letters

β, γ	= Dimensionless groups, $\beta = \epsilon_{po} D_A / D_{Aeo} \tau$, $\gamma = Q_M \rho_p / \epsilon_{po} \rho_q$
τ	= Tortuosity
θ	= Dimensionless time, $\theta_b = C_{Af}^k t / Q_M$, $\theta_p = C_{Ab}^k t / Q_M$
η	= Effectiveness factor
λ	= Ratio of critical solute-to-pore diameter, SD/PD
ρ	= Density, kg/m ³
ϵ	= Porosity ratio, $\epsilon_p / \epsilon_{po}$
$\epsilon_p, \epsilon_{po}$	= Porosities

Subscripts

A	= Main reactant
b	= Reactor bed
f	= Feedstock
o	= Initial conditions
p	= Catalyst pellet
q	= Coke

LITERATURE CITED

1. John, T.M.; Pachovsky, R.A.; Wojciechowski, B.W. Adv. Chem. Ser. 1974, 133, 422.
2. Voorhies, A., Jr. Ind. Eng. Chem. 1945, 37, 318.
3. Rudershausen, C.G.; Watson, C.C. Chem. Eng. Sci. 1954, 13, 110.
4. Ahmed, M.M.; Crynes, B.L. Prepr. Div. Pet. Chem. Am. Chem. Soc. 1978, 23, 1376.
5. Sooter, M.C. Ph.D. Thesis, Oklahoma State University, Stillwater, 1974.
6. Minaeu, V.Z. et al. Chem. Tech. Fuel Oils, 1975, 7, 436.
7. Kawa, W. et al. Prepr. Div. Fuel Chem. Am. Chem. Soc. 1974, 18, 215.
8. Prasher, B.D.; Gabriel, G.A.; Ma, Y.H. Ind. Eng. Chem. Process Des. Dev., 1978, 17, 266.
9. Masamune, S.; Smith, J.M. AIChE J. 1966, 12, 384.
10. Chiou, M.J.; Olson, J.H. Prepr. Div. Pet. Chem. Am. Chem. Soc. 1978, 23, 1421.
11. Froment, G.F.; Bischoff, K.R. Chem. Eng. Sci. 1961, 16, 189.
12. Crynes, B.L. U.S. DOE DE-14876-8, 1981.
13. Satterfield, C.N.; Colton, C.K.; Pitcher, W.H., Jr. AIChE J. 1973, 19, 628.

Figure 1. Coke Profiles in the Trickle Bed Reactor for Four Experimental Runs.

Figure 2. Average Coke Content Over the Reactor versus Time On Stream.

Figure 3. Catalyst Activity versus Average Coke Content Over the Reactor.

Figure 4. Most Frequent Pore Diameter versus Catalyst Coke Content.